

1 Disperse Systems, Colloidal Systems and their Classification

1.1 Common Feature of Dispersions

We use the words, disperse systems and colloidal systems, without giving a clear distinction between them. Depending on the type of emphasis on the properties, the same system can be called either a disperse or colloidal system. For instance, if the physical properties of a system are to be specifically discussed, it may be called a disperse system, but when chemical properties, industrial applications, or the historical backgrounds are emphasized they may be called colloids. At any rate, the disperse nature is indispensable also to colloids.

It is well known that an important feature of disperse and colloidal systems commonly appear to be the large ratio of surface area to volume of the dispersed or colloidal particles. The large ratio naturally appears for small particles, fibers, and thin films, as a physical state. In order to accomplish this state, a chemical agent called a surfactant may be needed. The large area is usually associated with large positive surface energy, but a surfactant, if present at the surface, can reduce the surface energy. In particular, in order to make a disperse system out of two immiscible liquids, a surfactant is required unless the mixture is violently shaken. This requirement has promoted research on surfaces in colloid chemistry. It is understandable that the stability of a colloid or a disperse system greatly depends on the surface conditions.

Atoms and molecules on the surface of a particle have different environments from those inside of the particle as they are exposed to the dispersion medium on the outside. Atoms and molecules in bulk phases are surrounded isotropically by similar atoms and molecules and, statistically, no net force is acting on them. When they are on the surface the force is not isotropic and some work is required to bring local atoms and molecules from the bulk to the surface. This is the positive surface energy which increases if new surface area is created. Since reactions usually occur in the direction of reducing the free energy of the system, the particles try to spontaneously reduce their total surface area by aggregating together to form larger particles. In such a case, disperse systems could be thermodynamically unstable unless the surface conditions are changed by a surfactant.

Of course, if small particles are charged in the same way, they can hardly get close to each other because of the repulsive Coulombic force, and remain as small particles.

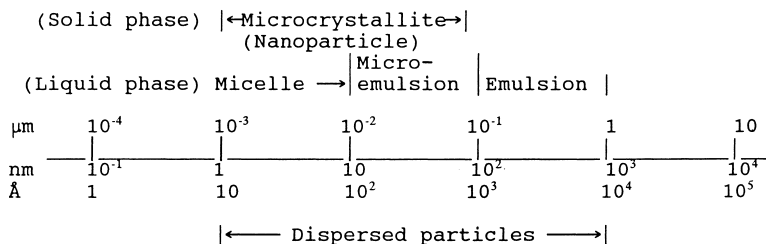


Fig. 1.1 Particle size classification.

In disperse systems, particles must be of small size, so that they can be subject to Brownian motion. The disperse systems are reasonably uniform and isotropic even under gravity in thermal equilibrium. Thin membranes, which could be colloids, must be excluded from being treated as disperse systems if their areas are large. Figure 1.1 illustrates the size classification.

If particles are smaller than about 1 nm, they may make a pure solution with the dispersion medium. The number of atoms in the nanoparticles is very small and the particles behave like usual molecules. However, if the solution is unstable, the particles are more likely to permanently increase the size by aggregation (or coagulation).

1.2 Particle Size and Chemical Bonding

Particles are made of atoms, but, the detailed internal structure related to how atoms are bound to each other in particles or, more specifically, how the bonding depends on the particle size is not well understood. However, there have recently been many computer calculations on the physical and chemical structures of small solid particles of group IIA and IIB (alkaline earth) elements. The computed particle size covers up to about 250 atoms, as discussed below.

Qualitatively, we can speak of the various types of chemical bonds. As long as an atom is isolated, it may remain as an electrically neutral closed entity. But, when the atoms gather together in a cluster size, they strongly perturb their electronic energy state of one another. Some (metallic) atoms find that they are in a lower free energy state by making their most loosely bound electrons spontaneously free to move within the particle. This internal ionization contributes to the binding of the atoms as a whole (metallic bonds). Or, in some cases, binding of the nearest neighboring atoms occurs by a mechanism in which each pair of them share two electrons of opposite electronic spins (a covalent bond). Another type of bond occurs if two neutral atoms have very different values of electronegativity or electron affinity. In this case, one electron can be energetically transferred from one to another atom, converting themselves to a pair of a positive and

a negative ion. They can thereby attract each other by the Coulombic force (an ionic bond). The binding energy due to the above mechanism is about a few to 10 eV per bond ($\sim 10^3$ kJ/mol).

On the other hand, if two atoms are far apart, or, their electrons are relatively tightly bound to their own nuclei, the atoms are subject to a mutual attraction by the so-called van der Waals' interaction which obeys an inverse sixth law. Classically speaking, the origin is considered to be due to an instantaneous dipole-dipole interaction. The binding energy due to this interaction is usually small, being of the order of 0.1 eV per bond (~ 10 kJ/mol); the binding is a physical nature.

These bonds or interactions among atoms usually occur simultaneously. Each of them partially contributes to the chemical or physical binding. Classically, the mixture of the contributions can be understood only in terms of probability. The most probable type of bond depends on the kind of atoms and the distance between them. All of these interactions, though classically stated above, can only be well understood in terms of quantum mechanics. This is because the de Broglie wavelength (given by Planck's constant/momentum), estimated by the classical model of the orbiting atomic electrons involved in the interactions, is not small compared with the geometrical size of the classical orbits. The geometrical size of the orbits of the free electrons in metallic bonds is estimated by the period of the periodic boundary conditions

Among the types of bonds, only metallic bonds can supply free electrons inside a particle. These free electrons make the particle electrically conductive. Otherwise, electrons are localized and particles will be poor conductors. This could happen even when particles are made of metallic atoms as described below.

Satoko (1987) measured the atomic distances in particles of various metallic atoms as a function of the particle size, by observing fine structures of the x-ray absorption spectra (EXAFS), as shown in Fig. 1.2. We know that an alkaline earth atom such as a calcium or a magnesium atom has two valence *s* electrons (the electron configuration s^2) outside the closed shells in the isolated ground state. The two *s* electrons belong to the closed *s* subshells so that their electrons are rather tightly bound and show quasi-closed-shell characteristics. Thus, calcium and magnesium elements form diatomic molecules, Ca_2 and Mg_2 , by van der Waals' bonding (Reuse et al., 1990 and Delaly et al., 1992). If they form a small cluster of size of about a few nm, the bonding character still remains to be of a van der Waals' type. However, if the cluster size increases, the number of atoms in the cluster increases. The overall disturbance on each atom becomes large and can strongly change the electronic orbital motion. Namely, the *s* electrons start to move in *sp* hybridized orbitals. Accordingly, as the cluster size increases, the bonding gradually changes to a covalent type (see Fig. 1.2) and the atomic distances decrease. But, the covalent bonds can be easily saturated and if the total number, *n*, of atoms in the cluster increases ($n=100\sim 200$), atoms seem to be bound by metallic bonds with an increasing bond length (Glossman et al., 1992). The minimum bond length occurs at the cluster size of about 10 nm.

On the other hand, alkali atoms with a single *s* electron outside their closed shells form covalent bonds in the small cluster, as expected from their diatomic bonding scheme like in O_2 and H_2 . However, if the particle size increases, a gen-

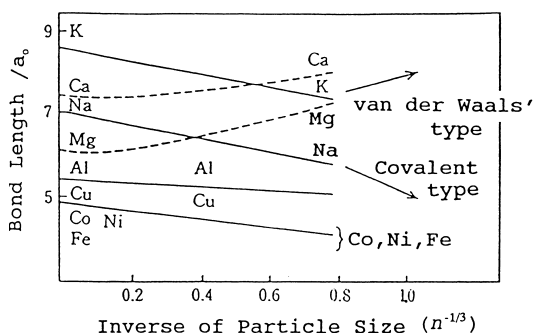


Fig. 1.2 The interatomic distances (bond lengths) of metals in the Bohr unit (a_0) versus the inverse of the particle size ($n^{-1/3}$, n : the number of atoms in a cluster) (Satoko, 1987, with permission from Springer-Verlag).

eral trend of increasing bond length will occur, like the large Mg clusters. This increasing bond length suggests a decreasing number density of atoms in the larger cluster.

Raghavachari and Rohlfing (1988) theoretically treated the structure of a silicon cluster (Si_n , $n=9,10$). A silicon atom has an electron configuration of s^2p^2 outside the closed shells, if isolated. But in a cluster it forms a hybridized orbital of $s^{2-x}p^{2+x}$. The value of x depends on the location of the silicon atom in the cluster. In the calculation, they assumed various possible atomic configurations in the cluster. They found that the value of x was nearly 0 for a silicon atom at the surface of the cluster, being closer to an isolated atom. But, $x \rightarrow 0.5$ as it approaches the center of the cluster. (In a bulk structure, $x=1.0$.) In addition, there was a trend of a slightly ionic structure in the cluster. Namely, the average location of electrons moved from the outside to the inside of the cluster, implying that a charge separation occurs within the cluster; in that the outer part is positively charged while the inner part is negatively charged. In contrast, no charge separation occurs in solid silicon.

Haberland et al. (1990) measured the ionization potential of mercury clusters. A mercury atom has an electron configuration of s^2 (forming a closed s subshell),

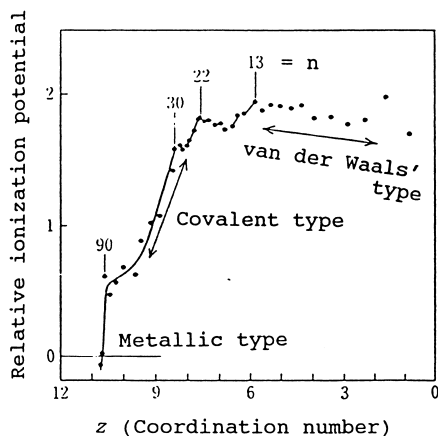


Fig. 1.3 The ionization potential of mercury clusters Hg_n . (Relative ionization energies as a function of the average coordination number z . $z=1$ for Hg_2 (Haberland, et al., 1990, with permission from ACS).

so that its molecule, Hg_2 , is a van der Waals' molecule, just like Ca_2 and Mg_2 . The bonding scheme is nearly the same as that of Ca and Mg, covering the large range of the cluster size. Thus, the ionization potential of the cluster of size less than about 30 atoms, for which the bonding is of a van der Waals' type, was observed to be constant and nearly the same as that of the isolated mercury atom. If the size was greater than 100 atoms, the ionization potential was again constant and nearly the same as that of the metallic mercury, as seen in Fig. 1.3.

1.3 Classification of Two-phase Disperse Systems

The above discussion was directed to small solid or liquid particles. Gas bubbles in liquid behave like particles, exhibiting Brownian motion. Thus, we can have various combinations of gas, liquid, and solid as a dispersed phase or a medium in a disperse system. We are historically very familiar with any of the combinations, so that each combinations carry individually specific names as illustrated in Table 1.1.

In particular, dispersions in which the medium is solid are becoming increasingly important in the field of material science (see, for example, Evans and Langdon, 1976). Aerosols are very often composed of rather large particles with a gaseous medium and the theoretical concepts to describe their behavior differ quite significantly from those with a liquid medium (see for instance, Davies, 1966; Hidy and Brock, 1970-72; Liu, 1976; and Chapt. 14).

There is another way of classification of colloidal systems from a functional view point. Freundlich (1926) suggested two classes, called lyophilic (solvent loving) and lyophobic (solvent fearing).

If the dispersion medium wets the particle, the system is called lyophilic. Otherwise, the system is lyophobic. Of course, a list covering a complete range of intermediate types has been revealed, but the terminologies are phenomenologically still useful. The distinction between them depends on the operational nature.

Table 1.1 Examples of two-phase systems

Dispersed phase/medium	Name	Examples
Liquid/gas	Liquid aerosol	Fog, liquid spray, mist
Solid/gas	Solid aerosol	Smoke, dust
Gas/liquid	Foam	Soap foam
Liquid/liquid	Emulsion	Milk, mayonnaise
Solid/liquid	Sol, suspension	Au sol, paste, gel
Gas/solid	Solid foam	Expanded polystyrene
Liquid/solid	Solid emulsion	Opal, pearl
Solid/solid	Solid suspension	Alloy, pigmented plastics

Namely, lyophilic systems are thermodynamically stable, but lyophobic systems are unstable. In the former (lyophilic) case, the disperse system occurs spontaneously when the solvent is added to the particles. The latter (lyophobic) case includes the system of oil and water. The mixture can be vigorously mixed to form a nontransparent, heterogeneous mass; but, on standing, the mixture will separate into two clear, homogeneous layers.

There are surface-active substances (surfactants) that can change a lyophilic to a lyophobic interface or vice versa. An example is a soap. Soap molecules have two active parts: the hydrophilic (water loving) part, which is an ionic group with a strong electrostatic attraction to water molecules, and another part (hydrocarbon), which is hydrophobic (water fearing) but is lyophilic and wets oil. If soap molecules cover the surface of an oil drop in water, the hydrophobic disperse system becomes a hydrophilic system. If the particles are solvated, then the solvent, immobilized at the surface, must be treated as a part of the particle.

Polar groups are not necessarily hydrophilic when attached to a long hydrocarbon (hydrophobic) chain (Laughlin, 1981). Water molecules in contact with hydrocarbons are oriented with a definite orientation to avoid hydrogen bonding with counter parts. The oriented water molecules have an orientational correlation, decreasing the entropy. This arrangement increases the free energy (Helmholtz' s free energy $A=U-TS$) of the system, raising a tendency of rejecting hydrocarbons from bulk water. Thus, it needs work to introduce a hydrocarbon chain into bulk water (28 dyne/cm times the contact area, Takeo et al., 1984). The oriented water molecules may be revealed by observing the electrostatic field produced by them (Takeo, 1993). Hydrophilic molecules, on the other hand, seem to have a disordering effect.

The term hydrophobic bonding has been used to describe the enhanced attraction between two particles in water if the water-particle interaction is weaker than water-water interaction. In this case, the particles orient water molecules in contact with them and the entropy reduction makes the system hydrophobic. When two of such particles come close to each other, since a reaction tends to occur in the reduction of the free energy, the oriented water molecules flow into the bulk water. Thus, the attraction is larger than that in free space and of a long range (Christenson et al., 1989, 1990). Therefore, the hydrophobic attraction could be much larger than what is predicted by the van der Waals interaction.

Strictly speaking, the origin of the hydrophobic interaction is not known yet. There is as yet no satisfactory theory of the interaction because of the complexity of the problem, though a number of promising theoretical approaches have been proposed (Nicholson and Parsonage (a review), 1982; Luzar et al., 1987; Ben-Naim, 1980; Israelachvili, 1991; Schrader and Loeb, 1992).

Exercises

- 1.1 Calculate the surface area-to-volume ratio for a spherical particle of a radius of 10 nm, 100 nm, or 1 μm . Why is it important for this ratio to be large for disperse systems?
- 1.2 In a simple model of metallic structure, each atom is considered, due to mutual interactions, to contribute one electron, which is more or less freely moving within the volume of the metal. How can this model predict the stability of the metal?
- 1.3 When atoms are bound by van der Waals' interaction, the interaction potential energy considered must have a minimum. Consider Lennard-Jones 6–12 potential ($\alpha/r^{12} - \beta/r^6$, r being the distance between the interacting pair). This potential is assumed not to be affected by the presence of other atoms in the neighborhood or in between the pair. When three atoms of the same kind are interacting between any pair and located on a line, find the minimum distance between any pair. Is there any force acting on them? How much does the distance differ if there are only two atoms?
- 1.4 Suppose that a charge separation occurs in a cluster of radius a , by transferring electrons from the outer to the inner region just like in a Si cluster. Otherwise, the cluster is neutral everywhere. Assume that the cluster is divided into two uniform regions. Each atom in the outer region loses 0.29 electrons on the average and each of the inner atoms gains 0.1 electrons on the average. What is the total electrostatic energy due to the charge separation? Consider that the atomic volume is v irrespective of the ionization conditions.
- 1.5 The free energy of a surface is positive, since the creation of the surface requires an energy. What would happen if the free energy is negative?
- 1.6 Suppose that water molecules are ordered in orientation when in contact with hydrophobic molecules. How is this ordering related with the entropy of the system? Explain with an example.
- 1.7 If the hydrophobic interaction is solely entropic, how is the force between two hydrophobic molecules in water related with the entropy change?

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